Division of Materials Chemistry
- Inorganic Photonics Materials -

http://noncry.kuicr.kyoto-u.ac.jp/

Prof
YOKO, Toshinobu
(D Eng)

Assoc Prof
TAKAHASHI, Masahide
(D Sc)

Assist Prof
TOKUDA, Yomei
(D Eng)

PD
MENAA, Bouzid
(Ph D)

PD
YAO, Jianxi
(Ph D)

PD
KAKIUCHIDA, Hiroshi
(D Eng)

PD
KANG, Eun-Seok
(Ph D)

Students

ZHANG, Jian (D3)
MASAI, Hirokazu (D3)
MIZUNO, Megumi (D2)
IKAWA, Hiroyuki (M2)
HIDAKA, Kenji (M2)
OHTANI, Shoichi (M1)
MAEDA, Takahiro (M1)
MIYAMOTO, Ayako (M1)
KOUNO, Ryou (UG)
SUZUKI, Masaru (UG)
FUJII, Masao (UG)
FUKUDA, Masahiro (RF)
FUKUDA, Masaaki (RF)
KUNIYOSHI, Minoru (RF)
TOMOYOSHI, Yoshio (RF)

Visitor

Prof INNOCENZI, Plinio University of Sassari, Italy, 24 September 2004

Scope of Research

In this laboratory, amorphous and polycrystalline inorganic materials with various optical functions such as photorefractivity, optical nonlinearity and photocatalysis are the target materials, which are synthesized by sol-gel, multi-cathode sputtering, melt-quenching and sintering methods. In order to obtain highly functional materials the structures are investigated by X-ray diffraction techniques, high-resoluction NMR, thermal analysis, various laser spectroscopies and ab initio molecular orbital calculations.

Research Activities (Year 2004)

Presentations

Na environment in sodium silicate glasses by ^{23}Na MQMAS NMR spectroscopy and ab initio MO calculation, Tokuda Y, Takahashi M and Yoko T, XX International Congress on Glass, Japan, 16 September - 1 October.

Photochemical reactions responsible for photorefractive index change in germanosilicate glasses, Takahashi M, Tokuda Y, and YOKO T, ibid.

Organic-inorganic hybrid low-melting glasses for photonics applications, Takahashi M, Tokuda Y, and Yoko T, ibid.

Relationship between viscoelastic properties and structure of organic-inorganic hybrid glass and supercooled liquid consisting of $R_{4-m}SiO_{m/2}$ units, Kakiuchida H, Takahashi M, Masai H, Tokuda Y, and Yoko T, ibid.

Preparation and properties of organic-inorganic hybrid low-melting glass films, Bouzid M, Takahashi M, Masai H, Tokuda Y, and Yoko T, ibid.

Reaction of phosphoric acid and chlorosilane as an acid-base pair for the formation of organic-inorganic hybrid low-melting glasses, Mizuno M, Takahashi M, Tokuda Y, and Yoko T, ibid.

Effect of the organic groups on the formation of siloxane network through sol-gel melting method, Masai H, Takahashi M, Tokuda Y, and Yoko T, ibid.

Low-power density laser fabrication of microstructures in low-melting glass doped with rare earth ions as an ionic heater, Takahashi M, Saito M, Kakiuchida H, Tokuda Y, and Yoko T, International conference on photoexcited and photoactivated processes, Lecce, Italy, 4 - 10 September.

Low-melting hybrid siloxane glasses containing very small amounts of silanol and alkoxy groups, Masai H, Takahahsi M, Tokuda Y and Yoko T The American Ceramics Society Glass and Optical Materials Division Meeting incorporating the XIV International Symposium on Non-oxide glasses and Novel Optical Glasses, Cape Canaveral, USA, 7 - 12 November.

Topics

Laser Micro-fabrication of Organic-inorganic Hybrid Low-melting Glasses Doped with Rare Earth Ions as an Ionic Heater

A new family of low-melting glasses has recently been reported by our group. The organic-inorganic hybrid low-melting glass of SnO-$Me_2SiO_{2/2}$-P_2O_5 system can be prepared through the non-aqueous acid-base reaction, in which the glass network linkages are produced by Lewis acid-base reaction between H_3PO_4, or H_3PO_3 as Lewis acid and $Si(CH_3)_2Cl_2$, $SnCl_2$ or other metal chloride as Lewis base. The obtained glasses showed a high optical transparency and high solubility of organic dyes and optically active ions. Therefore, this glass system is expected to be one of the potential candidate materials for active optical devices. We demonstrated the laser micro-fabrication of the low-melting hybrid glasses doped with neodymium ion (Nd^{3+}) by photo-induced refractive index change initiated by a low-power density cw Ar^+ laser. During this process the irradiated part is locally heated up above their melting temperatures, and then cooled down by turning off the laser beam, resulting in the fictive temperature or local structure of the irradiated region different from that of the non-irradiated part. The photoinduced refractive index change was estimated to be of the order of $\Delta n = -2\times10^{-3}$ with a MZ interferometer. Moreover, we have succeeded in fabricating waveguide or phase grating structures inside the hybrid low-melting glass as shown in Fig.1.

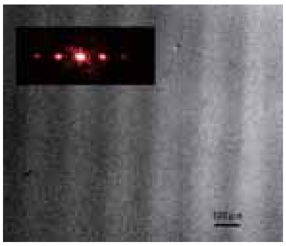

Figure 1. Phase grating structure written inside the low-melting glasses by laser heating through nonradiative phonon emission of an excited rare earth ion. Inset shows the diffraction of He-Ne laser light by the phase grating. (The higher order diffractions are also clearly observed)

Inhomogeneous Distribution of Na Ion in Mixed Alkali Silicate Glass

We have investigated local structure of Na ion in sodium silicate glasses and mixed alkali silicate glasses by means of ^{23}Na multiple quantum magic angle spinning (MQMAS) NMR spectroscopy and *ab initio* molecular orbital (MO) calculation. The ^{23}Na MQMAS NMR spectra of Na_2O-$2SiO_2$ have shown an inhomogeneous distribution of local structures around Na as shown in Fig. 2. The MO calculations on the model clusters of sodium silicate glass (Fig. 3) have indicated that there are both the crowded and isolated Na sites in sodium silicate glass. We have also investigated the local structure around Na in mixed alkali silicate glasses, $(Na_2O\cdot K_2O)\cdot 2SiO_2$. ^{23}Na MQMAS spectra of these glasses have also shown that the addition of K ion makes Na ion occupy more ionic site in mixed alkali silicate glasses. The present study suggests that a cation with a higher ratio of charge to ionic radius tends to aggregate in mixed silicate glasses.

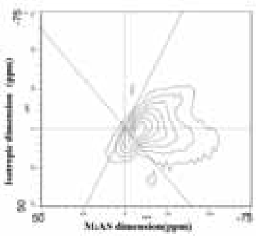

Figure 2. ^{23}Na MQMAS spectrum of Na_2O-$2SiO_2$ glass. MAS dimension and isotropic dimension are presented in ppm relative to an external reference of 1 mol/L NaCl solution. Inset two lines represent chemical shift (QS) and quadrupolar interaction shift (QIS).

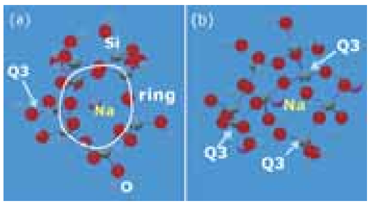

Figure 3. Optimized clusters modeling (a) isolated Na ion and (b) crowded one. The calculated chemical shifts of model (a) and (b) are 566.2 and 566.6 ppm, respectively. The quadrupolar shifts are calculated as 0.5 and 3.2 ppm for model (a) and (b), respectively. All these calculations were performed at the HF/6-31G* level.

Preparation of organic-inorganic hybrid polysiloxane low-melting glasses with high transparency in the uv region, Kuniyoshi M, Takahashi M, Tokuda Y and Yoko T, ibid.

Grants

Yoko T, Photochemical reactivity of glasses, Grant-in-Aid for Scientific Research (A) (2), 1 April 2001 - 31 March 2005.

Yoko T, Preparation of organic-inorgaic hybrid low-melting glasses through asid-base reaction, Asahi Glass Foundation, 1 April 2004 - 31 March 2005.

Yoko T, Optical measurement of glass transition temperatures, New Glass Forum, 1 April 2002 - 31 March 2004.

Takahashi M, Development of photorefractive low-melting glasses, Grant-in-Aid for Scientific Research (B) (2), 1 April 2001 - 31 March 2005.

Takahashi M, Inhomogeneous structures in the glasses, Grant-in-Aid for Scientific Research for Encouragement of Young Scientists (A), 1 April 2004 - 31 March 2006.

Takahashi M, Development of photonics materials based on the organic-inorganic hybrid low melting glasses, PRESTO, Japan Science and Technology Agency, 1 November 2002 - 31 March 2005.

Takahashi M, Murata Scientific Foundation, 1 July 2004 - 31 June 2005.

Yao J, Preparation of porous TiO_2 electrodes by photo-induced phase separation technique, Grant-in-Aid for Scientific Research for JSPS Researcher, 1 April 2004- 31 March 2005.